# Thermally poled germanosilicate films with high second-order nonlinearity

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**Abstract:** Accurate measurements of the second-order nonlinearity profile of thermally poled low-loss germanosilicate films grown on fused-silica substrates are reported, of interest as potential electro-optic devices. After optimization, we demonstrate a record high nonlinear coefficient $d_{33} \approx 1.6$ pm/V, a two-fold improvement over highest reported $d_{33}$ value in fused silica that we attribute to the presence of germanium.

**OCIS codes:** (310.6860) Thin films, optical properties; (190.4400) Nonlinear optics, materials

## 1. Introduction

Thermal poling is one of the most reproducible and widely used techniques to induce a stable second-order optical nonlinearity in glass. Some of the important potential applications of thermally poled glass include integrated electro-optic phase and amplitude modulators or parametric oscillators.[1] Poled glass exhibits significant advantages compared to existing nonlinear materials, including low loss, broad transmission bands, high optical damage threshold, and compatibility with fiber technology. The largest reported peak nonlinear coefficient for thermally poled silica glass is $d_{33} \approx 0.8$ pm/V.[2] As a result of this relatively weak nonlinearity, all poled-glass devices reported to date require fairly high voltages and/or long lengths. For this technology to become practical, the strength of the induced nonlinearity has to be improved.

In this letter, we show that the nonlinear coefficient can be doubled by doping the glass with germanium. After optimizing the material composition and poling conditions, we report a record peak $d_{33}$ coefficient of ~1.6 pm/V in thermally poled germanosilicate films. These films are of interest primarily for two important reasons: (1) their propagation loss can be very low,[3] which makes them excellent waveguide materials with a refractive index close to that of silica, and (2) the addition of Ge to the silica matrix increases the third-order optical susceptibility $\chi^{(3)}$ of the glass, which should result in an increase in the induced nonlinear coefficient. These properties make poled germanosilicate films a promising candidate for future low-loss integrated electro-optic devices.

Table 1. Characteristics of different germanosilicate films poled in air at ~5 kV and ~280 °C.

| *Sample #* | *Germane flow rate* | *Mole fraction of $GeO_2$ (%)* | $\frac{\chi^{(3)}_{Ge:SiO_2}}{\chi^{(3)}_{SiO_2}}$ | *Refractive index at 1064nm* | *Thickness* | *Poling time* | *Peak $d_{33}$ (pm/V)* |
|---|---|---|---|---|---|---|---|
| 1 | 0 sccm | 0 | ~1 | 1.469 | 4 μm | 10 min | 0.54 |
| 2 | 33 sccm | ~20 | 1.54 | 1.497 | 4 μm | 5 min | 0.80 |
| 3 | 33 sccm | ~20 | 1.54 | 1.497 | 4 μm | 10 min | 1.59 |
| 4 | 33 sccm | ~20 | 1.54 | 1.497 | 4 μm | 15 min | 1.00 |
| 5 | 33 sccm | ~20 | 1.54 | 1.497 | 2 μm | 10 min | 1.02 |
| 6 | 50 sccm | ~30 | 2.22 | 1.514 | 4 μm | 10 min | 0.78 |
| 7 | 90 sccm | ~56 | 4.77 | 1.553 | 4 μm | 10 min | 0.81 |

## 2. Germanosilicate thin film growth process

Germanosilicate films were deposited on fused-quartz substrates (Infrasil, 25 x 25 x 0.15 mm) by plasma-enhanced chemical vapor deposition (PECVD) using a parallel-plate reactor (Plasmalab 8510C). The films were grown at 350 °C and a pressure of 1 Torr at an RF power of 10 W at 13.56 MHz applied to the plates. The precursor gases were silane (2% $SiH_4/N_2$), germane (2% $GeH_4/He$), and nitrous oxide ($N_2O$). The flow rates of silane and nitrous oxide were kept constant at 180 and 225 sccm, respectively, while that of germane was changed from run to run between 0 and 90 sccm. The growth rate of the films was ~40 nm/min.

Annealing is almost always required to reduce the propagation loss of the optical waveguides that utilize CVD-grown silicon-based layers as the core. Recently, we have reported the lowest propagation loss values for as-grown germanosilicate films without the need for thermal annealing.[3] In order to optimize the poling process for this material, we grew seven individual germanosilicate films with different characteristics, as listed in Table 1. Based on our previous work,[3] the propagation losses of the as-grown waveguides were estimated to be less than 0.15 dB/cm at 1550 nm.

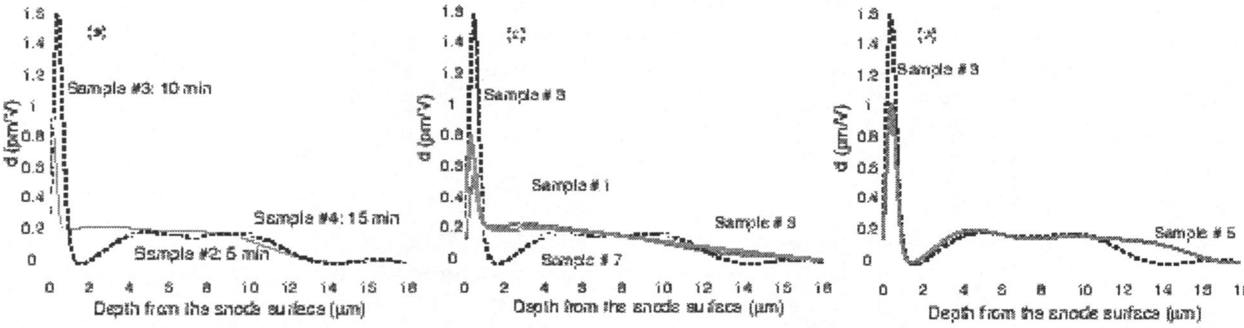


Fig. 1. The recovered nonlinearity profiles of (a) samples #2, #3, and #4; (b) ) samples #1, #3, #6 and #7; (c) samples #3 and #5.

## 3. Thermal poling results

The grown germanosilicate-Infrasil structures were thermally poled using polished *n*-type silicon electrodes (the positive electrode facing against the germanosilicate layer) in air at ~5 kV and 280 °C. The poling time was varied between 5 and 15 min (see Table 1) to investigate its effect on the peak nonlinear coefficient and maximize this coefficient. The nonlinearity depth profile of each poled sample was then measured by the Maker fringe-Fienup technique.[2] A fundamental laser beam at 1064 nm was focused onto the sample and the second-harmonic (SH) power generated within the poled region was recorded as a function of the beam incidence angle.[4] In order to avoid total internal reflection at the output face of the Infrasil substrate, and hence achieve high incidence angles (e.g. >85°) a pair of half-cylinders made of Infrasil was clamped on both sides of the poled samples.[5] The resulting Maker fringe (MF) curve was then corrected first for angle-dependent multiple reflections arising in the film from the refractive index mismatch between the film and the substrate, and second for Fresnel reflections at both the fundamental and the SH wavelengths occurring at the boundary between the input half-cylinder and the film and at the film–substrate boundary. Finally, the corrected MF curves were processed using an iterative Fourier transform technique[2] to uniquely retrieve the induced nonlinearity depth profile $d_{33}(z)$, where $z$ is the depth into the sample measured from the anode surface. For want of space, the measured MF curves of the samples are not shown here. The recovered nonlinearity profiles for the seven poled samples of Table 1 are shown in Fig. 1. The results in Fig. 1 are grouped according to the poling conditions and film properties. Figure 1(a) shows the profiles of samples #2, #3, and #4, all of which have a 4-μm thick germanosilicate films grown at a 33-sccm germane flow rate. To identify the optimum poling time, these nominally identical samples were poled under identical conditions except for the poling time, which was 5 min for sample #2, 10 min for sample #3, and 15 min for sample #4. As shown in Fig. 1(a), the profiles recovered for these three samples exhibit similar features, namely a sharp peak centered about 0.5 μm below the anode, followed by a weak pedestal that is approximately constant to a depth of ~9–12 μm and that gradually decreases to zero at a depth of 13–16 μm. This result reveals that the optimum poling time for these germanosilicate-Infrasil structures at an applied E-field of ~32.5 MV/m is ~10 min, corresponding to sample #3. The peak $d_{33}$ coefficient obtained under these poling conditions is as high as ~1.6 pm/V. To our knowledge, this is the highest second-order optical nonlinear coefficient measured without any ambiguities in a thermally poled germanosilicate glass. The peak $d_{33}$ coefficients measured for poling times of 5 and 15 min are ~0.8 pm/V and ~1.0 pm/V, respectively. As physically expected, as the poling time is increased from 5 min to 15 min the depth of the pedestal gradually increases from ~9 μm to ~12 μm (see Fig. 1(a)). The total depth of the induced nonlinear region (~13–16 μm) in Fig. 1(a) is significantly narrower than for bulk Infrasil samples thermally poled under similar conditions, for which the depth is typically ~40 μm.[2] Furthermore, unlike in thermally poled Infrasil, the $d_{33}(z)$ profile of the poled germanosilicate-Infrasil structures does not change sign. We believe that the reason for these differences is that the germanosilicate film limits the diffusion of positive ions such as $H_3O^+$ from the anode surface into the sample, which results in the formation of a narrower depletion region within the film and hence a shallower overall nonlinear region. A similar blocking behavior in germanosilicate films, which also resulted in narrower nonlinear widths, has been reported by others.[6]

After optimizing the poling time, we investigated the effect of the germane flow rate on the induced nonlinearity profile. For this purpose, we poled samples #1, #3, #6, and #7, which all have a 4-μm thick germanosilicate film but were grown at different germane flow rates, namely 0, 33, 50 and 90 sccm, respectively, so that their Ge concentrations were different (see Table 1). All four samples were poled under identical conditions, i.e., in air at ~5 kV and 280 °C, for 10 min. The recovered nonlinearity profiles for these samples are shown in Fig. 1(b). The profiles exhibit the same overall shape as the previous samples (see Fig. 1(a)). The peak $d_{33}$ coefficients of samples #1, #6 and #7 are 0.54, 0.78 and 0.81 pm/V, respectively. This investigation shows that the highest peak $d_{33}$ coefficient (1.6 pm/V) is achieved for a germane flow of 33 sccm (sample #3). However, a higher germane flow rate produces a higher Ge concentration and thus a higher $\chi^{(3)}$ (see fourth column of Table 1, where the listed $\chi^{(3)}$ values were calculated from the measured dispersion curves of the samples), so based on this argument alone we expect that the highest peak $d_{33}$ should occur at the highest flow rate. The fact that the peak $d_{33}$ coefficient is maximum in the 33-sccm sample suggests that the built-in field drops at higher Ge flow rates. We mostly relate these observations to an increase in the film electrical conductivity as the Ge concentration increased, which has been previously confirmed.[7] On the other hand, the built-in field of the 33-sccm sample is higher than that of the 0-sccm sample (pure $SiO_2$), although the latter has a lower electrical conductivity. This points out that there should be an optimum electrical conductivity range for a given set of poling conditions. This hypothesis is supported by the observation that under similar poling conditions, Suprasil, which contains much less impurity than Infrasil and thus has a lower conductivity, develops a built-in field nearly one order of magnitude lower than Infrasil.[1]

Finally, we investigated the effect of the film thickness on the induced nonlinearity profile. For this purpose, we poled sample #5, grown at a 33-sccm germane flow rate to a final thickness of 2 μm, for 10 min. Figure 1(c) shows the nonlinearity profile recovered for this sample. For comparison, the nonlinearity profile of sample #3, which was grown at the same flow rate and poled under identical conditions but is thicker (4 μm), is also shown in Fig. 1(c). The two samples have very similar profiles, which was expected since they have the same composition and were poled under the same conditions. However, the total depth of the nonlinearity is larger for sample #5 (~17 μm) than for sample #3 (~13 μm). A probable explanation for this difference is that the thinner 2-μm germanosilicate film in sample #5 acts as a weaker barrier for ion diffusion than the 4-μm film in sample #3. Furthermore, we believe that this charge spreading is at the origin of the weaker peak $d_{33}$ coefficient in sample #5 (1.02 pm/V vs. 1.6 pm/V in sample #3).

## 4. Summary

We have reported a detailed study of the nonlinearity profile of thermal poled germanosilicate films grown on fused-silica substrates by PECVD. This study sheds a better understanding on the physics of thermal poling in germanosilicate films. Inferred profiles all exhibit a sharp peak ~0.5 μm beneath the anode surface, followed by a weaker pedestal of roughly constant amplitude down to a depth of 13–16 μm. Compared to thermally poled undoped silica, they are shallower and do not exhibit a sign reversal, which indicates that the germanosilicate film significantly slows down the injection of positive ions from air into the glass. After optimizing the Ge concentration, the film thickness, and the poling time, we obtained a record peak $d_{33}$ coefficient of 1.6 pm/V in the sample grown at a 33-sccm germane flow rate (~20 mole% $GeO_2$) and poled for 10 min. Combined with the low propagation loss of these films, this enhanced nonlinearity makes poled germanosilicate films a promising candidate for planar electro-optic devices.

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